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14. ABSTRACT
The dissociative recombination of $C_3D_7^+$ was measured in the ion storage ring CRYRING.. The higher mass separation offered from the deuterated species provided more accurate branching ratios than the data obtained previously for $C_3H_7^+$. We obtained rate constants of $2.3\pm0.4 \times 10^{-7}$ cm^3 s^{-1} for $C_3D_7^+$ and $5.8\pm1.1 \times 10^{-7}$ for $C_4D_9^-$.

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Rate constants and branching ratios for the dissociative recombination of $C_3D_7^+$ and $C_4D_9^+$

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The dissociative recombination (DR) of hydrocarbon ions has been studied extensively at ion storage rings the past couple of years.[1–9] These studies have allowed complete product branching ratios to be determined in addition to thermal rate constants, which can also be obtained by means of afterglow techniques.[10,11] There are several reasons for this recent activity. There is a need for DR product branching ratios for hydrocarbon ions in several different areas of applied research. These include plasma assisted combustion,[12] thermonuclear reactor divertors,[13] and interstellar[14–16] and planetary astrophysics.[17] The studies carried out thus far demonstrate that the electron recombination induces considerably more molecular dissociation than expected, which results in the production of more free radicals per recombination event than previously believed. The grid technique developed at ion storage rings[1] has allowed the study of increasingly complex molecular ions.

In this note, we report data for the DR of $C_3D_7^+$ and $C_4D_9^+$ obtained in the ion storage ring CRYRING. In an earlier study, the rate coefficient and product branching ratios for the dissociative recombination of $C_3H_7^+$ was measured at CRYRING.[3] The analysis of the branching ratios was complicated, and we had reasons to believe that a study of one of the isotopomers $C_3D_7^+$ would provide more accurate branching ratios because of the higher mass separation offered from the deuterated species. This turned out to be correct.

In conjunction with this experiment, $C_4D_9^+$ was also studied. The hope was to be able to extract information on not only the C–C fission which had been studied elsewhere,[7] but also the deuterium release channels. This turned out to be impracticable, and we report here on the C–C bond breaking only, in addition to the thermal rate constant.

The experiments were carried out at the ion storage ring CRYRING, operated by the Manne Siegbahn Laboratory of Stockholm University. The grid technique applied to branching ratio measurements in CRYRING has been described in detail[1,3,4] and we give only a brief description here. By a suitable choice of precursor molecules, deuterated 1-bromopropane (secondary-C_3D_7–Br) and *t*-butylbromide (tertiary-C_4D_9–Br), *s*-$C_3D_7^+$ and *t*-$C_4D_9^+$ isomers were produced using a Nielsen hot-cathode discharge ion source. The ions were injected into CRYRING and stored at the maximum energies possible, 1.9 MeV and 1.45 MeV, respectively. Dissociative recombination reaction products were generated in the 0.85 m interaction region, where the ions were merged with a collinear electron beam. The neutral products were detected ≈4 m downstream from the interaction region by an energy-resolving surface barrier detector. Branching ratios were measured by placing a grid of known transmission in front of the surface barrier detector. Figure 1 shows a pulse-height spectrum for $C_3D_7^+$ taken with this configuration. Without the grid, all combinations of DR products

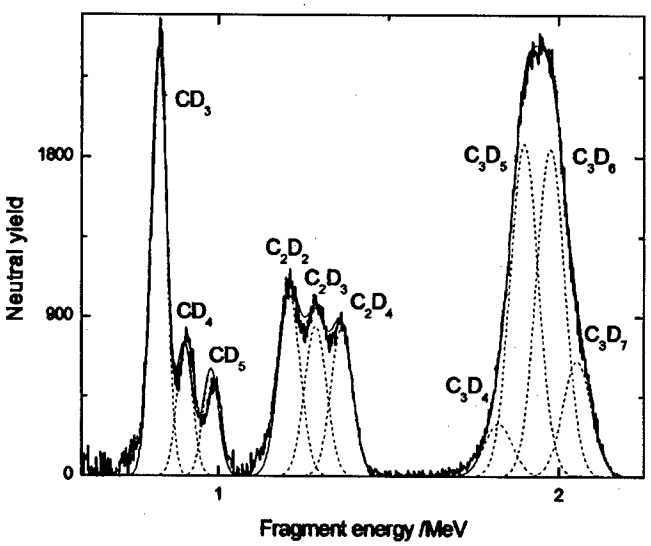

FIG. 1. Pulse-height spectrum for $C_3D_7^+$ with the grid placed in front of the surface barrier detector.

TABLE I. Thermal rate constants for $C_3D_7^+$ and $C_4D_9^+$.

Species	Rate Constant at 300 K (10^{-7} cm^3 s^{-1})	$(300/T)^n$ n	Other 300 K results (10^{-7} cm^3 s^{-1})	References
s-$C_3D_7^+$	2.3±0.4	0.73	(19, 8.3)[a]	3, 22
t-$C_4D_9^+$	5.8±1.1	0.59	8.3[a]	18

[a]Results for the hydrogeneted isotopomers.

yield a pulse corresponding to the maximum beam energy. With the grid, some of the products can be blocked from the detector, and a pulse at a fraction of full energy is obtained. The spectrum of the pulse-height vs energy is related to the product branching ratios via a probability matrix equation.[4]

DR cross sections were measured by varying the electron velocity over a broad range with respect to the ion velocity while counting the DR products impinging on the detector with the grid removed. Since the electron and ion beam currents can be measured, and the interaction length is known, absolute cross sections were obtained and converted to thermal rate constants by integrating the cross section assuming a Maxwell distribution of reactant velocities at a given temperature.

Thermal rate constants are shown in Table I. The DR rate constants for $C_3D_7^+$ and $C_4D_9^+$ differ by about a factor of 2 at 300 K, and have slightly different electron temperature dependences. The results for $C_3D_7^+$ and $C_4D_9^+$ are lower than those from flowing afterglow measurements on the hydrogenated isotopomers.[18] The same trend was noted for $C_2H_5^+/C_2D_5^+$[19,20] and H_3O^+/D_3O^+.[21] There is significant disagreement with the previously reported CRYRING data[3] for $C_3H_7^+$, larger than one would anticipate from the isotope effect. A prerequisite for the determination of an absolute cross section is that the ion current can be measured, which is difficult with small intensity hydrocarbon ion beams. The procedure used in Ref. 3, which was based on a two-step normalization of the signal, might have introduced a larger error than anticipated at the time. The two-step normalization procedure was unique to the $C_3H_7^+$ experiment due to a malfunctioning piece of equipment. In contrast, a new and very sensitive integrating current transformer was used in the present experiment.

In Table II the branching ratios for DR of $C_3D_7^+$ and $C_3H_7^+$ are given. The higher resolution afforded by the deuterated isotopomer made it possible to determine all decay channels. The disagreement with $C_3H_7^+$ concerning the single H(D)-atom loss channel is due to the inferior resolution for $C_3H_7^+$. The carbon bond breaking fractions, which can be measured with the same accuracy for the two isotopomers, differ slightly, which is likely to be an isotope effect.

The complete branching fractions could not be determined for $C_4D_9^+$ due to the resolution of the detector, and we had to settle with only determining the amount of C–C bond breaking. All three carbon bonds are preserved in 61% of the recombination events, while a CD_2-molecule is ejected in 39% of the events. This is in excellent agreement with results from the ASTRID ion storage ring.[7]

TABLE II. Product branching ratios in the dissociative recombination of $C_3D_7^+$ and $C_3H_7^+$.

Product channels for $C_3D_7^+$	$C_3D_7^+$ (%)	$C_3H_7^+$ (%)[a]
C_3D_6+D	13±5	42
C_3D_5+D_2	12±5	
C_3D_5+D+D	22±8	11
C_3D_4+D_2+D	9±2	9
C_2D_4+CD_3	3±2	
C_2D_4+CD_2+D	0	4
C_2D_3+CD_4	2±2	
C_2D_3+CD_3+D	15±4	19
C_2D_2+CD_4+D	3±3	
C_2D_2+CD_3+D_2	21±4	11
C_3D_3+D_2+D_2	0	
C_2D_6+CD	0	<5
C_2D_5+CD_2	0	
Total C–C breaking	44	34–39

[a]Reference 3.

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